

Low Temperature Growth of In_2O_3 and InN Nanocrystals on Si(111) via Chemical Vapour Deposition Based on the Sublimation of NH_4Cl in In

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Abstract Indium oxide (In_2O_3) nanocrystals (NCs) have been obtained via atmospheric pressure, chemical vapour deposition (APCVD) on Si(111) via the direct oxidation of In with Ar:10% O_2 at 1000 °C but also at temperatures as low as 500 °C by the sublimation of ammonium chloride (NH_4Cl) which is incorporated into the In under a gas flow of nitrogen (N_2). Similarly InN NCs have also been obtained using sublimation of NH_4Cl in a gas flow of NH_3 . During oxidation of In under a flow of O_2 the transfer of In into the gas stream is inhibited by the formation of In_2O_3 around the In powder which breaks up only at high temperatures, i.e. $T > 900$ °C, thereby releasing In into the gas stream which can then react with O_2 leading to a high yield formation of isolated 500 nm In_2O_3 octahedrons but also chains of these nanostructures. No such NCs were obtained by direct oxidation for $T_G < 900$ °C. The incorporation of NH_4Cl in the In leads to the sublimation of NH_4Cl into NH_3 and HCl at around 338 °C which in turn produces an efficient dispersion and transfer of the whole In into the gas stream of N_2 where it reacts with HCl forming primarily InCl. The latter adsorbs onto the Si(111) where it reacts with H_2O and O_2 leading to the formation of In_2O_3 nanopyramids on Si(111). The rest of the InCl is carried downstream, where it solidifies at lower temperatures, and rapidly breaks down into metallic In upon exposure to H_2O in the air. Upon carrying out the reaction of

In with NH_4Cl at 600 °C under NH_3 as opposed to N_2 , we obtain InN nanoparticles on Si(111) with an average diameter of 300 nm.

Keywords Indium oxide · Indium nitride · Nanocrystals · Low temperature · Chemical vapour deposition

One of the fundamental building blocks necessary for the development of nanotechnology are semiconductor nanodots (NDs), nanocrystals (NCs) or nanoparticles (NPs) viz. quantum dots (QDs). These are completely quantised, zero dimensional (0D) semiconductors with discrete energy levels whose electronic and optoelectronic properties are size dependent. Semiconductor QDs have been traditionally obtained by strained layer growth using molecular beam epitaxy (MBE) or chemical vapour deposition (CVD) [1, 2]. However, during recent years NDs, NCs and NPs have also been obtained using complex chemical synthesis involving solid, liquid and gas reactions and a broad variety of methods including hydrothermal and colloidal synthesis. So far, NDs, NCs, NPs have been realised from group IV elemental semiconductors like Si [3, 4] and Ge [5] but also III-V and II-VI compound semiconductors like GaAs [6], InP [7, 8], InN [9] GaN [10], ZnS [11, 12], CdS [13] and oxides like ZnO [14–17], SnO_2 [18] and In_2O_3 [19–28]. Among the III-V's, nitride (N) semiconductors are especially attractive due to the fact that their energy band gap can be adjusted over a very wide range e.g. between 0.7 eV for InN up to 3.4 eV in GaN by changing the composition of the ternary semiconductor $\text{In}_x\text{Ga}_{1-x}\text{N}$ over $0 \leq x \leq 1$. On the other hand, among the oxides, In_2O_3 is a very important wide-band gap semiconductor ($E_G = 3.55$ eV) which is widely used for the fabrication of devices such as electro-optic modulators, solar cells, electro-chromic mirrors and sensors [29].

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To date In_2O_3 NCs have been obtained via CVD using $\text{In}_2\text{O}_3:\text{In}$ in a flow of $\text{Ar}:\text{CH}_4$ at 950 °C by Jia et al. [19] or just Ar between 950 and 1300 °C by Cheng et al. [20] and Guha et al. [21]. Similarly, chains of In_2O_3 NCs have been obtained by direct oxidation of In which was heated to 900 °C [25]. High yields are critical in order to successfully fabricate nano-devices and low temperatures desirable for compatibility with mainstream silicon processes but also those involving polymers. One of the shortcomings in the synthesis of In_2O_3 nanostructures obtained by CVD is the fact that until now high temperatures have been used. Low temperature synthesis of In_2O_3 NPs has been demonstrated via the sol–gel method by Zhou et al. [22], which took, however, >100 h and involved annealing between 500 and 850 °C. In addition, a high yield-low temperature synthesis of single crystalline tin doped indium oxide octahedrons via a low temperature, catalyst-free process was also demonstrated by Wei et al. [23], who obtained nanostructures as low as 450 °C using a solution of indium acetate and tin chloride. Therefore, there is active interest in the low temperature synthesis of In_2O_3 NCs and an active, growing interest in InN QDs which have been grown by MBE or metal organic CVD (MOCVD) predominantly on GaN, AlN, Al_2O_3 . Very few investigations have been carried out on the synthesis of colloidal InN NPs [9] while recently indium oxynitride which can be thought of as an alloy between InN and In_2O_3 was investigated and proposed for optoelectronic device applications [30].

In this work, we have investigated the synthesis of In_2O_3 NCs by direct oxidation of In with O_2 in an atmospheric pressure (APCVD) reactor and the limitations that arise as a consequence of the direct oxidation process. We find that during direct oxidation of In by O_2 the transfer of In into the gas stream is inhibited by the formation of an In_2O_3 shell around the In powder which melts at 157 °C. The In_2O_3 shell breaks up only at high growth temperatures (T_G) i.e. $T_G > 900$ °C, thereby releasing In into the gas stream which in turn reacts with O_2 leading to the formation of a high yield of In_2O_3 octahedrons with sizes of 500 nm but also chains of these nanostructures. No such nanostructures were obtained by direct oxidation for $T < 900$ °C. We find that including NH_4Cl into the In under a gas flow of N_2 leads to the sublimation of NH_4Cl into NH_3 and HCl at around 338 °C which results into the complete transfer of the In precursor into the gas stream of N_2 where it reacts with HCl and forms InCl that adsorbs onto the Si(111) and reacts with H_2O and O_2 forming In_2O_3 nanopillars at temperatures as low as 500 °C. Upon carrying out the reaction under NH_3 as opposed to N_2 we obtain InN nanoparticles with an average diameter of 300 nm. The low temperature growth of InN and In_2O_3 NCs directly on Si(111) using a common type of reaction

could be exploited for the synthesis of InN/ In_2O_3 hetero-nanostructures for a diverse range of applications such as solar cells, sensors, etc.

Experimental

The In-based nanostructures were grown using an APCVD reactor which consists of four mass flow controllers (MFC's) and a horizontal quartz tube furnace, capable of reaching a maximum temperature of 1100 °C. More specifically, we used n^+ Si(111) and n^+ Si(111) covered with a thin layer of Au that had a thickness of a few nm's. The Si(111) samples had an area of $\approx 1 \text{ cm}^2$ and initially they were immersed in HF, rinsed in de-ionised water and dried with nitrogen prior to the deposition of the Au layer in order to remove the native oxide and surface contamination. The Au layer was deposited via sputtering at a rate of 0.1 nm/s using an Ar plasma under a pressure $< 10^{-4}$ mBar. For the purpose of optical measurements all of the In-based NCs were grown directly on quartz.

In the case of direct oxidation at high temperatures, fine In powder (Aldrich, Mesh-100, 99.99%) was weighed and loaded into a quartz boat together with a Au/Si(111) and plain Si(111) sample. The Au/Si(111) sample was positioned about 5 mm over the In and the Si(111) about 10 mm downstream from the In powder. Then the boat was loaded into the quartz tube reactor and positioned directly above the thermocouple used to measure the heater temperature at the centre of tube. After loading the boat at room temperature (RT), Ar (99.999%) was introduced at a flow rate of 500 standard cubic centimetres per minute (sccm) for 10 min, in order to purge the tube. Following this, the temperature was ramped to the desired growth temperature (T_G) in a reduced Ar flow of 100 sccm. Upon reaching T_G the flow of Ar was reduced to 90 sccm and O_2 introduced at a flow of 10 sccm for another 60 min after which the O_2 flow was cut off and the quartz tube was allowed to cool down over at least 60 min in an inert gas flow of Ar, 100 sccm. The sample was removed only when the temperature was lower than 100 °C.

For the synthesis of In_2O_3 NCs at low temperatures, an equimolar mixture of In powder (Aldrich, Mesh-100, 99.99%) and NH_4Cl (99%, VWR) was prepared and loaded in the centre of the quartz boat. A Au/Si(111) sample was positioned over the mixture of In and NH_4Cl and a Si(111) sample without Au downstream from the mixture as described above. After loading the boat at room temperature (RT), nitrogen N_2 (99.999%) was introduced at a flow rate of 500 sccm for 15 min in order to purge the tube. Following this, the temperature was ramped to the desired growth temperature (T_G) in a N_2 flow of 100 sccm's. Upon reaching T_G the flow of N_2 was maintained at 100 sccm for

a further 60 min after which the quartz tube was allowed to cool down over at least 60 min. Finally the InN NCs were obtained by using an equimolar mixture of In:NH₄Cl and exactly the same growth conditions that led to the formation of InN nanowires by direct nitridation of In at 600 °C under a gas flow of 250 sccm NH₃ which is described in detail elsewhere [31].

The morphology of the nanostructures were examined with a TESCAN scanning electron microscope (SEM) and the crystal structure and phase purity of the nanostructures were investigated using a SHIMADZU, XRD-6000, X-ray diffractometer and Cu, K α source. A scan of θ – 2θ in the range between 10° and 80° was performed for the nanostructures grown under different conditions. For the XRD we used Al and stainless steel (Fe₃C) holders to place the samples on the goniometer. In some of the XRD patterns the characteristic peaks of the holder material were detected and identified. Finally, optical spectroscopy was carried out using a standard spectrophotometer UV/V (Perkin Elmer Lambda 950) in the reflection mode at near normal incident to minimise scattering effects from the sample.

Results

In the case of direct oxidation of In with O₂ we observed the formation of In₂O₃ NCs only for $T_G \geq 900$ °C and a typical SEM image of In₂O₃ NCs grown at $T_G = 1000$ °C is shown in Fig. 1a. Following the reaction we found that the In powder had expanded significantly into a porous like solid which disintegrated easily into a powder while a bright yellow dust corresponding to the In₂O₃ NCs was found on the Si(111) but also in plentiful supply on the sides of the quartz tube. The In₂O₃ NCs are octahedrons and had the tendency to form large dendrites consisting of In₂O₃ NC chains as shown in Fig. 1b and c, respectively. The small In₂O₃ NCs have a diameter of ≈ 500 nm, while the sizes of the larger octahedrons are almost ≈ 2500 nm.

The surface density of the In₂O₃ NCs across the surface of the Si(111) was very uniform and the density of the dendrites was dependent on the amount of In and the distance of the silicon from the In. The In₂O₃ NCs grown at $T_G = 1000$ °C on silicon exhibited clear peaks in the X-ray diffraction spectra shown in Fig. 2 and have a cubic structure, while the optical bandgap is near 3.5 eV as determined from the reflection spectrum shown in Fig. 3.

As already stated above, no nanostructures were obtained for $T_G < 900$ °C in the presence of O₂ and the In powder which melts at 157 °C forms a well-defined sphere in the quartz boat found after each growth run. The surface of the In had a grey, non-reflective appearance as opposed

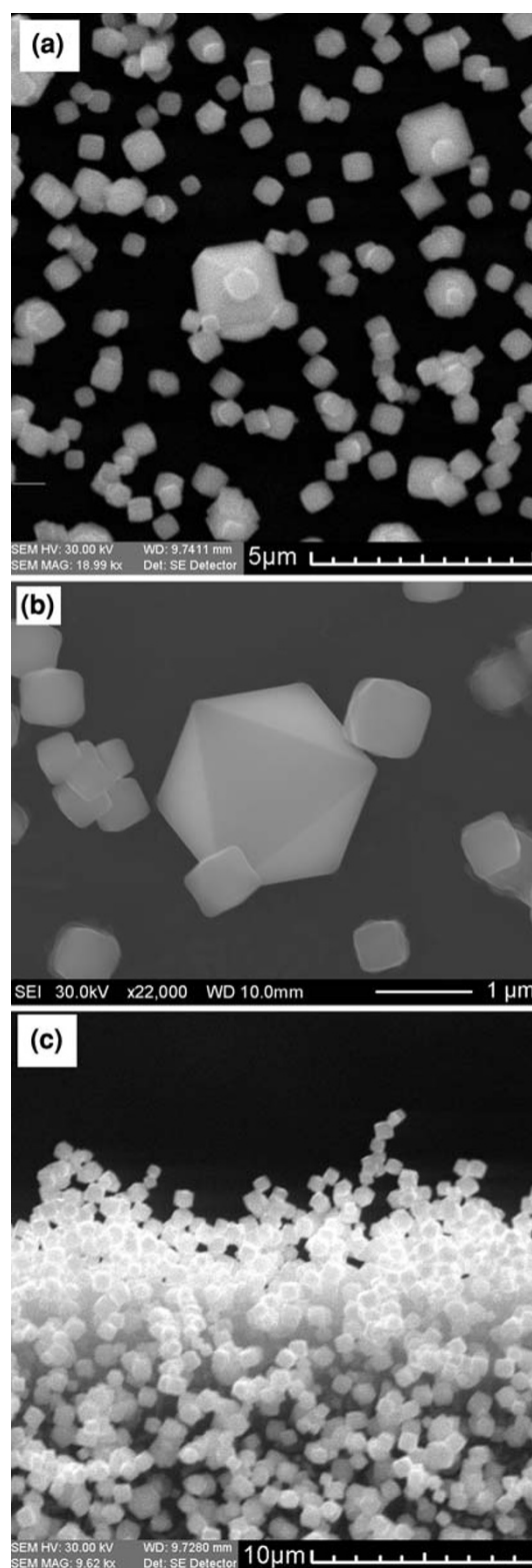


Fig. 1 In₂O₃ NCs grown on Si(111) by direct oxidation of In with O₂ at 1000 °C (a) Isolated NCs with min diameter of 500 nm (b) Dendrite structure consisting of chains of NCs (c) Side view of NC chains

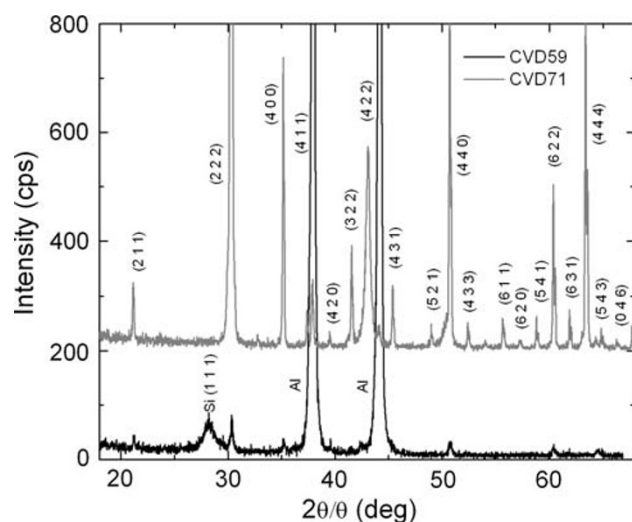


Fig. 2 XRD spectrum of In_2O_3 NCs grown on Si(111) (i) by direct oxidation of In by Ar:10% O_2 at 1000 °C, i.e. CVD71, top pattern and (ii) by reaction of In with NH_4Cl at 600 °C under a flow of N_2 i.e. CVD59, lower pattern. Enhanced In_2O_3 peaks are obtained from the sample grown at the higher temperature

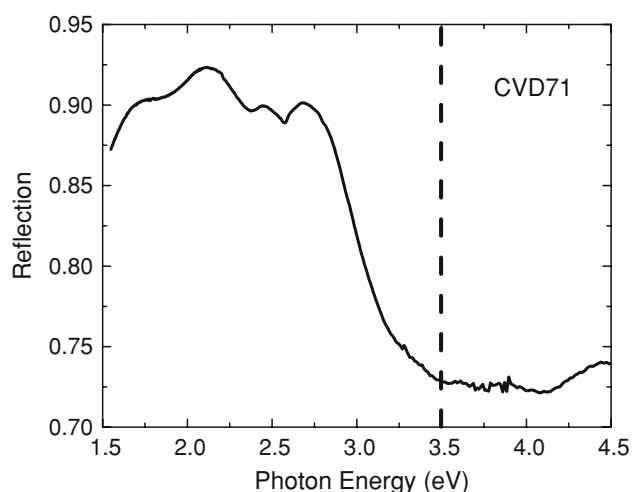


Fig. 3 Reflection spectrum of the In_2O_3 NCs grown at 1000 °C directly on quartz

to the highly reflective surface of In which we always obtained during the growth of InN from In and NH_3 [31].

In contrast to the above findings, the reaction of In and NH_4Cl occurred efficiently even at temperatures as low as 400 °C, since no trace of the In: NH_4Cl mixture whatsoever was found in the boat after removing the latter from the quartz tube. In addition, a dark yellow powder was always found near the cool end of the reactor which rapidly turned into metallic grey upon exposure to the ambient air.

A typical SEM image of In_2O_3 NCs obtained on Si(111) at 600 °C after the reaction of In with NH_4Cl under N_2 is shown in Fig. 4a. Larger In_2O_3 NCs were obtained at $T_G = 500$ °C, as shown in Fig. 4b. Interestingly, no

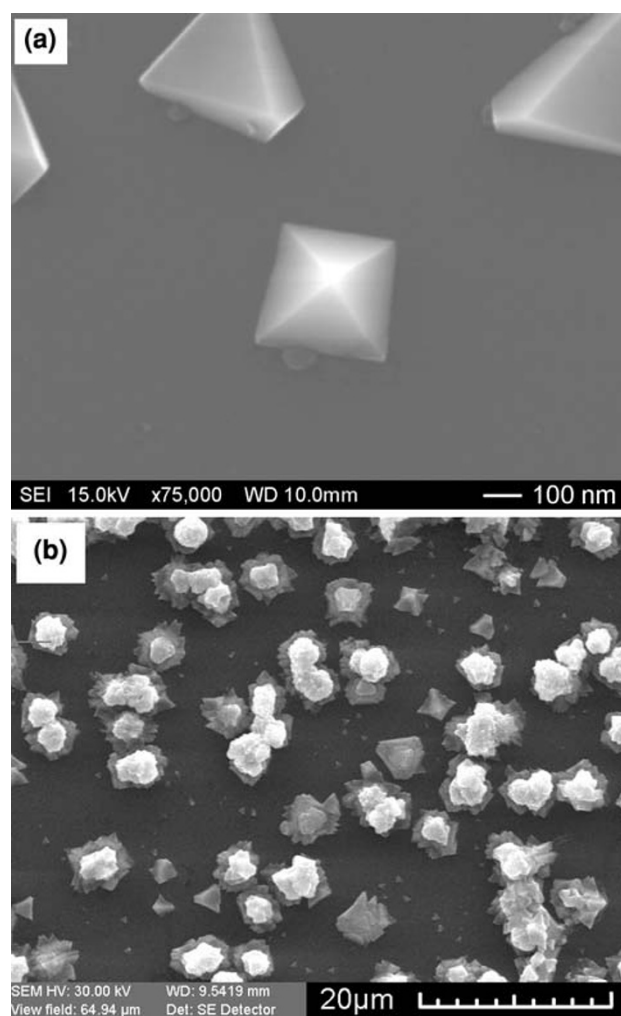


Fig. 4 (a) In_2O_3 NCs as small as 200 nm were grown on Si(111) at 600 °C via the reaction of In and NH_4Cl . The large pyramids have a base almost equal to 2000 nm (b) Coalescence of In_2O_3 NCs into small flower like structures at 500 °C

nano-pyramids were obtained on the Si(111) that was covered with a few nm's of Au and positioned directly over the In: NH_4Cl mixture.

Discussion

To date In_2O_3 NCs have been obtained using CVD either by direct oxidation of In or by reduction of In_2O_3 at high temperatures [19–21]. In the case of direct oxidation of In with O_2 a shell of In_2O_3 forms around the molten source of In. This shell inhibits the transfer of In into the gas stream, so it is necessary to increase the temperature above 900 °C in order to break the shell and ensure an adequate transfer of In into the gas stream. This leads to an apparent expansion of the In very similar to that which occurs during the nitridation of Al when it reacts with NH_3 . In the latter

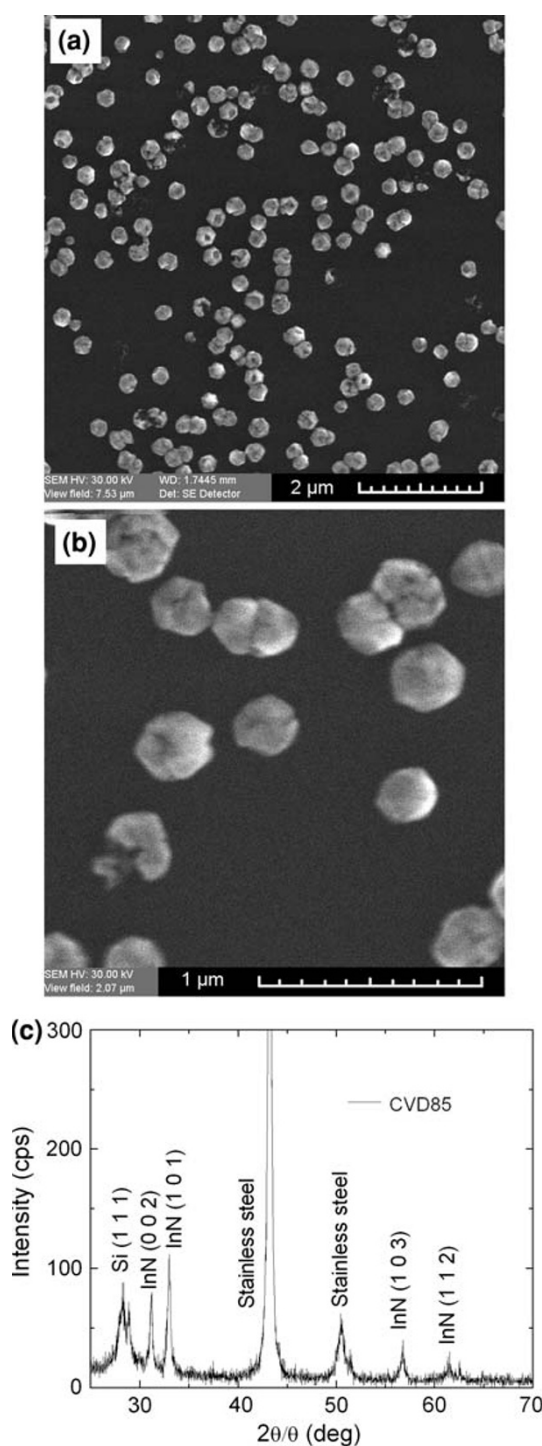
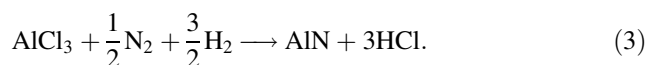
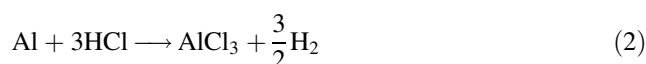


Fig. 5 (a) SEM image of the InN NCs grown at 600 °C on Si(111) (b) high magnification of the hexagonally shaped InN NCs with diameters 200–300 nm (c) XRD spectrum corresponding to single phase hexagonal InN

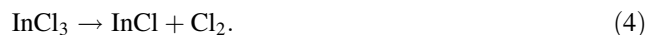
case, when Al is heated up in a flow of $N_2:NH_3$ it leads to the formation of AlN around the source of Al which in turn inhibits the transfer of Al into the gas stream and consequently the growth of AlN. At high temperatures the

molten Al expands and breaks the surrounding AlN shell thereby releasing Al. After cool down the residual Al appears to have expanded and has a porous like appearance. The formation of AlN on the Al source has been shown to be inhibited by incorporating NH_4Cl in the Al. The decomposition of NH_4Cl enhances the porosity of the Al melt thereby promoting the transfer of Al into the gas stream. On the other hand, the reaction of NH_4Cl and Al leads to the formation of $AlCl_3$ which is a gas and this reacts in turn with nitrogen giving AlN according to,



In the case of In, we find that incorporation of NH_4Cl leads to the complete transfer of the solids of In and NH_4Cl into the gas stream of N_2 . Indium has a low melting point of 156 °C and once molten it forms a sphere whose size depends on the initial amount of powder. The complete elimination of the In and NH_4Cl is a direct consequence of the sublimation of the NH_4Cl into NH_3 and HCl which occurs at 338 °C. According to Chaiken et al. [32], the sublimation rate of NH_4Cl increases by a factor of 10^4 when changing the temperature from $T = 100$ –600 °C and the typical sublimation weight loss of NH_4Cl is over 90% when heated for ≈ 60 min. Sublimation is endothermic and the temperature is expected to be reduced only by a few tens °C in the case of NH_4Cl [32].

Consequently, the sublimation of NH_4Cl enhances the porosity of the In resulting into an efficient transfer of In from the interior of the melt into the gas stream where it subsequently reacts with the HCl thereby forming InCl, InCl₂ and InCl₃. However, gaseous InCl₃ at temperatures >400 °C suffers decomposition and yields InCl and InCl₂ while the amount of InCl increases with increasing temperature [33]. Thus, during growth for $T > 400$ °C InCl₃ decomposes predominantly into InCl according to,



InCl is yellow, changes to red at 120 °C and has a relatively low melting point of 216 °C. The InCl molecules adsorb on the Si(111) surface and react with H_2O possibly absorbed by the NH_4Cl to form In_2O_3 NCs according to,



A similar reaction involving spraying of InCl₃. H_2O in ethanol was recently employed for the deposition of a polycrystalline thin film of In_2O_3 on stripe-patterned Si at 280 °C [34].

The In_2O_3 NCs have a stable, light yellow colour, even after exposure to the ambient air. However, most of the InCl is carried downstream as evidenced by the large amounts of dark yellow powder found only near the cool end of the reactor. Both InCl and InCl_2 decompose into In and Cl when reacting with H_2O and so lead to the separation of metallic indium. Therefore, the rapid change of the dark yellow powder to metallic grey upon exposure to the ambient air is attributed to the humidity of the air, i.e. H_2O . It is important to point out that the In_2O_3 NCs were also obtained via the sublimation of NH_4Cl in In under the presence of O_2 for $T < 900^\circ\text{C}$. In contrast, no In_2O_3 NCs were obtained in the case of the oxidation of In alone by O_2 for $T < 900^\circ\text{C}$. The formation of In_2O_3 pyramidal NCs on $\text{Si}(111)$ was confirmed by the XRD spectrum shown in Fig. 2. In both XRD spectra illustrated in Fig. 2, only the In_2O_3 reflections are observed ensuring the absence of a second phase. All In_2O_3 peaks in Fig. 2 correspond to the In_2O_3 peaks also observed by Du et al. [35] who have grown In_2O_3 structures by dehydration of $\text{In}(\text{OH})_3$ after heat treatment at 500°C for 4 h. The In_2O_3 peaks have higher intensities for growth temperatures above 600°C .

On the other hand, the sublimation of NH_4Cl in the In under a gas flow of NH_3 does not yield pyramidal NCs. Upon carrying out the reaction of In with NH_4Cl in a gas flow of 250 sccm of NH_3 as opposed to N_2 at 600°C [31] we obtained single phase, hexagonal structured InN NPs with an average diameter of 300 nm as shown in Fig. 5b and confirmed by XRD shown in Fig. 5c where the (002), (101), (103) and (112) reflections of the InN , $\text{Si}(111)$ and the stainless steel holder peaks are observed. In this case the InCl reacts with the NH_3 giving InN similar to the recent investigation of Kumagai et al. [36] on hydride vapour phase epitaxy of InN epitaxial layers via the reaction of InCl_3 with NH_3 . These InN NCs are also very similar in size and morphology with those obtained by MOCVD on GaN [2].

An interesting aspect of the In_2O_3 NCs obtained from the reaction of In with NH_4Cl is that they self-assemble into well-defined circles for $T \leq 600^\circ\text{C}$, as shown in Fig. 6a and coalesce near the periphery leading to the formation of μm size, flower-like structures, as shown in Fig. 6b at $T = 500^\circ\text{C}$ resembling a wreath. Upon reducing the temperature to 400°C we do not find anymore isolated In_2O_3 NCs but only μm size flower-like structures which now fill the wreaths, as shown in Fig. 6c. This type of self-assembly was not observed for the In_2O_3 NCs grown by direct oxidation of In with O_2 at $T > 900^\circ\text{C}$ which aggregate into dendrites that consist of NC-chains. A possible explanation for this type of self-assembly is wetting of the $\text{Si}(111)$ surface by In . The wetting is not uniform across the sample but instead the In forms wet circular regions on the $\text{Si}(111)$ surface which tend to

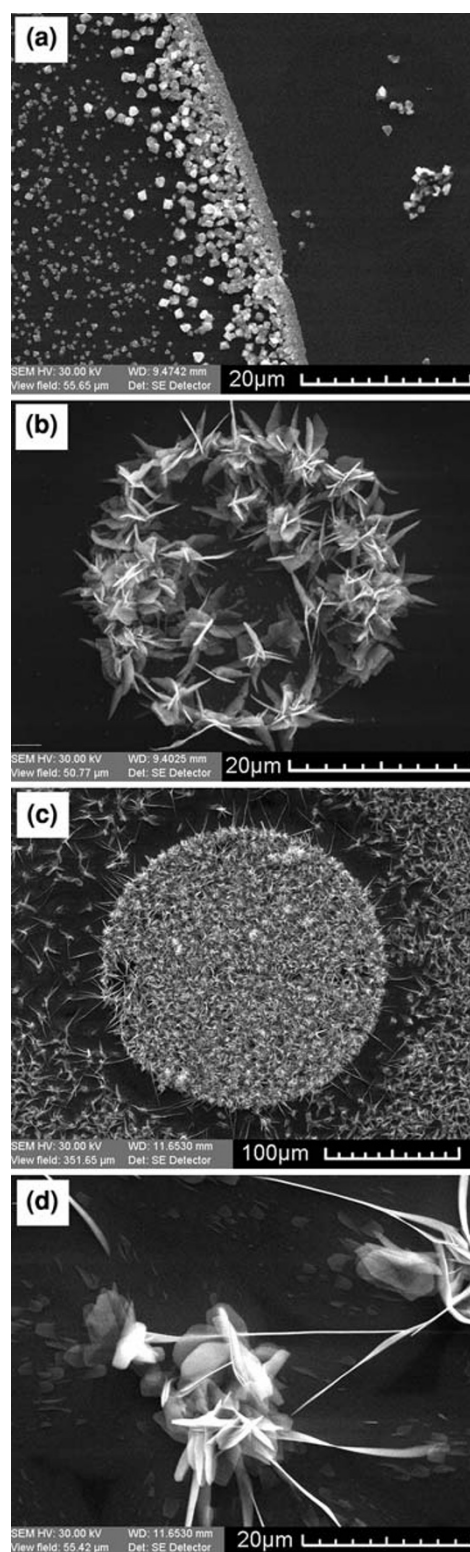


Fig. 6 **a** Coalescence of In_2O_3 NCs at the periphery of a well-defined circle and formation of flower-like structures **b** Coalescence of In_2O_3 NCs into 'flowers' and formation of a wreath spanning over $20\ \mu\text{m}$, obtained at $T_G = 500^\circ\text{C}$ **c** Large wreath full of flower-like structures spanning over almost $200\ \mu\text{m}$ obtained at $T_G = 400^\circ\text{C}$ and **d** $20\ \mu\text{m}$ isolated flower-like structure

expand as the growth proceeds thereby leading to the coalescence of the NCs and the formation of the wreath-like structures shown in Fig. 6a–d. These wreath-like structures become larger when decreasing the temperature and the individual flower-like structures may grow up to 20 μm , Fig. 6d.

Conclusion

We have investigated the synthesis of In_2O_3 NCs by direct oxidation of In with O_2 and also by the incorporation of NH_4Cl in the In under N_2 . The reaction of In and NH_4Cl yields InN NCs using NH_3 . The synthesis of In_2O_3 NCs by direct oxidation of In with O_2 is limited by the formation of an oxide shell surrounding the In which can be eliminated only at $T_G > 900^\circ\text{C}$ as a consequence of the expanding melt therefore allowing an efficient transfer of In into the main gas stream. At $T_G > 1000^\circ\text{C}$ we obtain 500 nm size In_2O_3 NCs but also dendrite structures consisting of NC chains.

The high temperature requirement can be alleviated by the addition of NH_4Cl into the In which breaks down into NH_3 and HCl by sublimation thus resulting into the complete transfer of the In into the gas stream and the formation of InCl which reacts with H_2O and O_2 . In this way we obtained In_2O_3 NCs at temperatures as low as 500°C under N_2 but also InN by simply changing from N_2 to NH_3 . This method is potentially interesting for the synthesis of narrow and wide-band gap InN and In_2O_3 NCs at low temperatures but also for nano-engineering of heterostructures and the fabrication of novel devices such as third generation solar cells.

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